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ELECTRONIC STRUCTURE OF METAL AND ALLOY SURFACES.(U)
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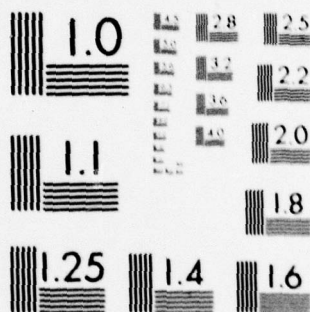
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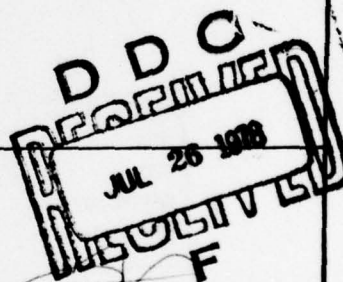
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particles, has the advantage that it can bridge the gap between solid-state band theory and molecular quantum chemistry, thereby permitting the elucidation of surface electronic structure as a function of local atomic arrangement and composition. The use of clusters also facilitates the representation of bulk and surface defect electronic structure, the study of chemisorption bonding, and ultimately the interpretation of surface chemical activity such as catalytic reactivity and corrosion. The recently developed self-consistent-field X-alpha (SCF-X α) approach to calculating the electronic structure of metallic and bimetallic aggregates is described along with illustrative applications to surface-related problems.

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ELECTRONIC STRUCTURE OF METAL AND ALLOY SURFACES

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Abstract

The electronic structure of metal and alloy surfaces is central to the understanding of the physical and chemical properties of such surfaces. However, progress in calculating surface electronic structure from first principles has lagged behind that of calculating bulk band structure because of the difficulty of applying the conventional band description at an interface. The theoretical study of the electronic structure of finite metallic and bimetallic clusters representing local surface and bulk atomic configurations, including small particles, has the advantage that it can bridge the gap between solid-state band theory and molecular quantum chemistry, thereby permitting the elucidation of surface electronic structure as a function of local atomic arrangement and composition. The use of clusters also facilitates the representation of bulk and surface defect electronic structure, the study of chemisorption bonding, and ultimately the interpretation of surface chemical activity such as catalytic reactivity and corrosion. The recently developed self-consistent-field X-alpha (SCF-X α) approach to calculating the electronic structure of metallic and bimetallic aggregates is described along with illustrative applications to surface-related problems.

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INTRODUCTION

Over the last few years there has been a rapid growth of interest in developing quantitative theories for the physical and chemical properties of metal and alloy surfaces. This has been stimulated, in part, by the technological importance of heterogeneous catalysis and corrosion in energy production and conversion and, in part, by the development of ultra-high-vacuum optical and electron spectroscopic techniques for characterizing surfaces and chemisorption thereon.¹

In the development of theories for surface electronic structure and chemisorption, a number of different approaches may be taken. The one following directly from solid-state physics is to consider a semi-infinite solid or "slab" with or without an ordered overlayer of chemisorbed atoms or molecules.^{2,3} The system is assumed to be perfectly periodic in two dimensions, and energy-band theory is modified to permit the calculation of surface states. Unfortunately, because of the loss of periodicity perpendicular to the surface, the implementation of this technique is difficult and costly in required computer time. This approach also has the disadvantage that localized surface defects and the effects of disorder cannot be straightforwardly included within the framework of the model. Since chemisorption is fundamentally a localized surface phenomenon, involving adsorbate bonding to one or at most a few surface atoms, an alternative theoretical model is to construct metal-adsorbate complexes (so-called "surface molecules"), analogous to metal-ligand coordination complexes of inorganic and organometallic chemistry. Real-space methods of quantum chemistry, e.g., molecular-orbital theory, can then be used to calculate the local electronic structures and related properties of these

complexes. The analogy between metal-surface adsorbate complexes and metal coordination complexes is not fortuitous. Significant progress has been made recently in the synthesis of molecules containing several transition-metal atoms coordinatively saturated by a variety of ligands.⁴

A useful link between these two theoretical approaches is provided by the recently developed cluster representation of the electronic structure of solids.⁵⁻⁸ It has been demonstrated that for certain (not all) properties of bulk solids or surfaces, including those with localized defects, impurities, compositional and topological disorder, an adequate physical model consists of a finite number of atoms artificially removed from the infinite solid. This cluster of atoms is then treated within the framework of molecular-orbital theory. If one accepts for the moment that cluster models can provide useful information about certain properties of solids then the following highly desirable situation with respect to the two theoretical approaches mentioned above may result. One can perform calculations on inorganic and organometallic molecules, with the usual cross-checks with experiments, and from these studies draw conclusions about the nature of metal-ligand bonding. The same theoretical method can then be applied to clusters of various sizes interacting with the same ligands. In this way one can examine the way that the properties change as one goes from the case of a molecule to that of a finite cluster and finally, in the limit of a sufficiently large cluster, to the case of the infinite solid or surface. In this way one can hopefully obtain information to answer the crucial question which is implicit when one compares the two types of models, namely, in what ways are clusters (of a given size) similar to and in what ways are they different from the infinite solid as far as a given property is concerned.

In order to carry out a meaningful cluster calculation the constraints on the theoretical method chosen are quite severe. A minimum requirement if one wishes to compare results for the series which starts with an inorganic molecule and ends with a chemisorbed layer on an infinite surface is that these two endpoints be adequately treated within essentially the same method. If the same mathematical approximations are used throughout the study and if the method is trustworthy for the two extreme cases then one can be confident that the similarities and differences found between the clusters and either the solid surface or the isolated molecule are meaningful and not simply a result of differing computational approaches. More practical constraints also exist. If one wishes to study the convergence of a cluster model as a function of the size of the cluster then clearly the method chosen must be capable of treating sufficiently large clusters with a reasonable computational effort.

Fortunately the self-consistent-field- $X\alpha$ -scattered-wave (SCF- $X\alpha$ -SW) method^{9,10} satisfies at least these minimum criteria. It has been successfully used to study a number of inorganic complexes⁷ and has furnished valuable information on their electronic structure and spectra so that one is confident that an isolated molecule may be adequately treated. Moreover the SCF- $X\alpha$ -SW method is the discrete analogue of the Korringa-Kohn-Rostoker¹¹⁻¹³ method of band theory so that in the limit of the infinite solid SCF- $X\alpha$ -SW results go over into the results of a well-studied solid-state physics approach.

The $X\alpha$ -SW method is also sufficiently rapid that quite large clusters can be treated (see below) in modest amounts of computational time. The number of atoms required in a cluster model will of course depend on which properties of the solid are of interest. Clearly if one is interested for

instance in properties associated with the Fermi surface of a metal then very large (computationally intractable) aggregates would have to be considered. On the other hand if more local aspects of the solid are involved then one may hope that reasonably small clusters could be useful.

With all the above considerations in mind, we will review the results of SCF- $X\alpha$ -SW electronic-structure calculations on metallic and bimetallic clusters representing the bulk and surface environments of metals and alloys, including surface-adsorbate configurations. Most of the details of this work are published or in press elsewhere, so that the results will be described only briefly and qualitatively in this paper. The interested reader is referred to the cited references.

MOLECULAR-ORBITAL STUDIES OF ALUMINUM CLUSTERS CONTAINING UP TO 43 ATOMS

The self-consistent-field- $X\alpha$ -scattered-wave molecular orbital method has been used to perform electronic structure calculations for two series of aluminum clusters containing up to 43 atoms, the largest metal cluster so far treated by this method.¹⁴ The first series consisted of clusters of 13, 19, and 43 atoms having the O_h symmetry characteristic of bulk fcc aluminum while the second consisted of 5, 9, and 25 atom clusters having the C_{4v} symmetry appropriate to the (100) surface. The convergence of the calculated results as a function of cluster size has been examined. The largest cluster of each series yields an occupied band width of over 90% [92% (C_{4v}), 99% (O_h)] of the bulk band width derived from X-ray emission spectra. These larger clusters also show reasonable agreement with the main features of density of states curves derived from band structure calculations and those inferred from recent photoemission measurements. The differences and similarities between various cluster and band theory results have been

established. Examination of projected densities of states for the various atoms provides a possible explanation of the smaller occupied band width observed in the photoemission spectrum, compared with the X-ray or band structure results. It is also suggested that similar projected density of states plots for the case of transition metal clusters might prove useful for the study of structure sensitivity in heterogeneous catalysis.

CLUSTER MOLECULAR-ORBITAL STUDIES OF OXYGEN

CHEMISORPTION ON ALUMINUM

SCF- $X\alpha$ -SW molecular orbital calculations have been performed for clusters of 5, 9, and 25 aluminum atoms representing the (100) surface in interaction with one, four, or five oxygen atoms at various positions above, in, and below the surface.¹⁴ Comparison of the results with recent ultraviolet and X-ray photoemission (UPS and XPS) results lend further support to the contention that at room temperature oxygen atoms are incorporated in or below the surface even at low exposure. Projected density of states curves for the 25 atom cluster with an oxygen atom centered in the first surface layer show three energy regions of significant oxygen character at about -9.5, -7, and -3 eV relative to the Fermi energy. Inspection of the wave functions for the corresponding levels shows that the -9.5 eV peak is due mainly to bonding combinations of in-plane oxygen p orbitals with aluminum s and p orbitals. The -7 eV peak arises from both in-plane and out-of-plane oxygen p orbitals, again in bonding combinations, while the orbitals responsible for the -3 eV peak are best classified as nonbonding with respect to aluminum-oxygen interactions. The two peaks at highest binding energy (-9.5 and -7 eV) have been observed in recent UPS experiments while at present there is only inconclusive evidence for the third, and it is therefore suggested that a detailed angle and photon energy dependent study be performed.

ELECTRONIC STRUCTURES OF TRANSITION- AND NOBLE-METAL CLUSTERS OF CATALYTIC IMPORTANCE

There is much current interest in the electronic structures of small transition- and noble-metal aggregates which constitute the active centers of heterogeneous catalysts. Metal aggregates less than 10 \AA in size, referred to as "clusters" in order to distinguish them from larger particles or crystallites, are of special importance because their electronic structures, catalytic properties, and interactions with supporting environments can, in principle, deviate from those characteristic of the bulk metals.

In recent publications,^{15,16} the electronic structures of small copper, nickel, palladium, and platinum clusters, as calculated by the self-consistent-field X-alpha scattered-wave (SCF-X α -SW) molecular-orbital method, have been described and compared with the results of similar calculations by semiempirical molecular-orbital methods. One is at first struck by the systematic similarities, rather than the differences, between the SCF-X α electronic structures of the clusters and those of the corresponding bulk metals. For example, the manifolds of orbital energy eigenvalues for 13-atom clusters having the cubo-octahedral nearest-neighbor coordination characteristic of the fcc lattice exhibit all the principal features of the bulk band structures, e.g., overlap of the "d band" by the "s,p band," a sharp peak in the density of states around the Fermi energy for the Ni₁₃, Pd₁₃, and Pt₁₃ clusters, increasing band width through this series, and magnetic spin polarization in the case of Ni₁₃.¹⁵ More recent SCF-X α studies of 4- and 6-atom nickel, palladium, and platinum clusters, including relativistic effects, indicate that even these small clusters exhibit most of the qualitative features of the crystalline band structure and can be utilized as a basis for understanding the nature of the interaction of hydrogen with these metals.¹⁶ These predictions

have been confirmed by spectroscopic studies of small noble- and transition-metal clusters isolated in inert matrices.

While a small transition-metal cluster does indeed exhibit most of the characteristics of the crystalline band structure, the molecular boundary conditions and the fact that most of the atoms of the cluster are effectively coordinatively unsaturated "surface" atoms lead to some important additional features of the electronic structure.¹⁵ These include the appearance of localized orbitals split off in energy from the top and bottom of the cluster d-orbital manifold, which can be interpreted as the cluster analogues of the "surface states" split off from the bulk d band for an extended crystalline surface. Also associated with the cluster boundary conditions is a buildup of electronic charge density in the cluster interior, compensated for by a depletion of electronic charge at the cluster periphery. Since a faceted polyhedral (e.g., cubo-octahedral or icosahedral) cluster is the simplest globular analogue of a "stepped" crystalline surface, the effective positive charge on the atoms at the cluster periphery is analogous to the positive charge observed at the catalytically active edge atoms of a stepped transition-metal (e.g., platinum) surface. The resulting electric field gradient at the cluster boundary, coupled with a high density of d orbitals spatially directed away from the coordinatively unsaturated atoms at the cluster periphery (see Fig. 17 of Ref. 15), can promote interaction and overlap of these orbitals with symmetry-conserving orbitals of adsorbates, catalytic-reactant molecules, and supporting environments. Thus the electronic structures of small transition-metal clusters not only mimic the band structures of the corresponding crystalline metals, but also have distinct features that may be key to understanding the active centers of heterogeneous catalysts and catalytically active sites (e.g., "steps") on otherwise ideal crystalline surfaces.

ELECTRONIC STRUCTURE, MAGNETIC PROPERTIES, AND
CATALYTIC ACTIVITY OF IRON CLUSTERS

Although nickel, palladium, and platinum clusters of the type studied in Refs. 15 and 16 are a logical starting point in the fundamental investigation of catalysts, other Group-VIII transition metals are of comparable catalytic versatility and invite theoretical consideration. Among these, iron is the most widely used commercial catalyst for the synthesis of ammonia (the Haber process), is used commercially as a catalyst in the Fischer-Tropsch synthesis of high-molecular-weight paraffins, and is generally one of the most surface-active transition metals. The electronic structures and related properties of iron clusters are also of intrinsic interest in the ways they compare with the band structure and physical properties of bulk crystalline iron. Of particular importance are the magnetic states of iron clusters, their relation to the ferromagnetism of crystalline iron, and the influence, if any, of such magnetism on the catalytic activity and surface reactivity of this metal.

SCF- $X\alpha$ -SW molecular-orbital calculations have therefore been carried out for a variety of iron clusters ranging in size from 4 atoms to 15 atoms. In this summary, we focus on the results for 9- and 15-atom clusters having the body-centered-cubic (bcc) geometry characteristic of the local atomic arrangement in bcc crystalline α -iron. The calculations were carried out in spin-unrestricted form, i.e., different orbitals for different spins, in precisely the same fashion as described for nickel clusters in Ref. 15.

From the qualitatively similar spin-polarized electronic structures of the Fe_9 and Fe_{15} clusters, one can extract the following characteristics which are directly comparable with the band structure of ferromagnetic crystalline α -iron.

- (1) The cluster electronic structures can be characterized in terms of manifolds of predominantly d-like spin orbitals bracketed in energy by orbitals which have significant s,p character in analogy to the overlap of the d band by the s,p band in bulk crystalline iron.
- (2) The Fermi level of each cluster passes through the center of the "spin-down" (\downarrow) d-orbital manifold in a fashion similar to the intersection of the Fermi level with the center of the "minority-spin" d band of ferromagnetic iron.
- (3) The exchange splitting and widths of the cluster d bands, particularly those for Fe_{15} , are comparable with the values for bulk ferromagnetic iron.
- (4) The cluster total density of states shows a pronounced two-peak structure, which is primarily a consequence of the exchange splitting, consistent with the density of states for ferromagnetic iron.
- (5) Bonding and antibonding cluster spin orbitals of t_{2g} and e_g symmetry have a spatial character similar to the energy eigenstates of ferromagnetic iron near the bottom and top, respectively, of the d bands.
- (6) The t_{2g}^{\uparrow} and e_g^{\uparrow} orbitals are the lowest unoccupied majority-spin states of the Fe_{15} cluster and are analogous to the majority-spin crystal eigenstates of ferromagnetic iron lying immediately above the Fermi energy.

SCF- $X\alpha$ calculations have also been carried out for a bcc Fe_9 cluster, in which the boundary conditions have been modified to simulate the "embedding" of the cluster in an extended crystalline environment. Although the correspondence between the cluster and crystalline electronic structures is somewhat improved, e.g., through an effective increase in the cluster d-band width, the main conclusions given above are essentially unaltered.

The cluster results can be further utilized as a basis for understanding the transition from collective ferromagnetism to "superparamagnetism" and local paramagnetism with decreasing particle size or increasing temperature. For example:

- (1) The average paramagnetic magneton numbers per atom for the Fe_9 and Fe_{15} clusters are 2.9 and 2.5, respectively, approaching the 2.2 value for ferromagnetic crystalline α -iron, whereas SCF- $X\alpha$ results for smaller iron clusters, such as Fe_8 and Fe_4 , suggest increasing magnetic moment approaching the atomic limit. The latter trend is supported experimentally by Mössbauer studies of very small iron aggregates isolated in inert matrices and may be contrasted with the theoretical and experimental observations that the magneton number decreases with decreasing cluster size for small nickel aggregates (cf. Ref. 15).
- (2) The partial-wave decomposition of the Fe_9 and Fe_{15} cluster spin orbitals indicates that the contribution of the 4s-like components to spin polarization, although relatively small in magnitude, is opposite in direction (antiparallel to) that of the dominant 3d-like components, in good agreement with the analysis of magnetic form factors in polarized neutron scattering data for crystalline iron.
- (3) Somewhat more spin density in the Fe_9 and Fe_{15} clusters is concentrated in the e_g orbitals than in the t_{2g} orbitals, providing a local model for the concentration of spin density along the [100] direction (the direction of easy magnetization) in crystalline α -iron, as deduced from neutron-diffraction measurements.
- (4) Neutron-diffraction studies of crystalline iron at temperatures greater than the Curie temperature T_c suggest that short-range ordering of spins in the form of "spin clusters" ($\sim 10 \text{ \AA}$ in size) persists well

into the paramagnetic region, and that the paramagnetic magneton number is approximately 25% greater than the value for ferromagnetic iron ($T < T_c$). It is obvious therefore that the electronic structure of crystalline iron in the paramagnetic region is more appropriately represented statistically by a local spin-polarized cluster model, than by the extended \vec{k} -space band-structure description, since the cluster electronic structure is not dependent on the assumption of long-range crystalline ordering of spins. Utilizing the bcc Fe_{15} cluster as a prototype model for a "spin cluster," one finds that the unoccupied spin orbitals, t_{2g}^{\uparrow} and e_g^{\uparrow} , in the ground state ($T = 0^\circ\text{K}$) are within a fraction of an eV of the Fermi energy, in analogy to the lowest unoccupied majority-spin eigenstates of ferromagnetic crystalline iron [see item (6) described above]. Thermally induced "spin-flip" electronic excitations from the Fermi level (which intersects the minority-spin manifold) to the lowest unoccupied t_{2g}^{\uparrow} and e_g^{\uparrow} orbitals for $T > T_c$ results in an effective 30% increase of cluster magnetic moment and magneton number, thereby providing a good model for the observed increase in magnetic moment of crystalline iron in the paramagnetic region. Such excitations only slightly alter the average exchange splitting and total density of states of the cluster, consistent with the apparent persistence of the local density of states for crystalline iron at $T > T_c$ (as measured, for example, by photoemission), an experimental observation which heretofore has been inexplicable within the framework of conventional ferromagnetic energy-band theory.

We can benefit from the large effective surfaces presented by the Fe_9 and Fe_{15} clusters to discuss the catalytic activity, selectivity, and general surface reactivity of iron aggregates, as has previously been done for nickel,

palladium, and platinum in Refs. 15 and 16. Among the manifolds of densely spaced d-orbital eigenstates of these clusters are levels which correspond to antibonding spin orbitals primarily localized on and spatially oriented away from the cluster periphery or "surface," especially in the general vicinity of the Fermi energy. Such spin orbitals have the proper spatial character for symmetry-conserving overlap with the orbitals (e.g., the π^* orbitals) of certain reactant molecules and are also likely to be present in abundance on the surfaces of catalytic iron aggregates and particles of more general morphology. This argument is further clarified by a direct comparison of the Fe_{15} cluster-spin-orbital energies with the SCF- $X\alpha$ molecular-orbital energies of N_2 , CO , and O_2 , the molecules which are key reactants in iron-catalyzed ammonia synthesis, Fischer-Tropsch synthesis, and surface oxidation.

SCF- $X\alpha$ orbital energy eigenvalues, because of their equivalence to derivatives of total energy with respect to occupation numbers,^{9,10} can be rigorously identified with differential orbital electronegativities which are a generalization of Mulliken's definition of electronegativity, namely, the average of the ionization potential I and electron affinity A . While the SCF- $X\alpha$ transition-state procedure⁹ leads to relaxed orbital energies that can be individually identified with I or A , the unrelaxed ground-state SCF- $X\alpha$ orbital energies define a set of orbital electronegativities which are a measure of the average electron donor and electron acceptor character of each orbital. For a spin-polarized system like the Fe_{15} cluster, the spin-orbital energy eigenvalues define a set of spin-orbital electronegativities. Thus the relative positions of the SCF- $X\alpha$ orbital energies of the Fe_{15} cluster and reactant molecules N_2 , CO , and O_2 , are a measure of the differences in orbital electronegativity among these components. To understand the relationship between spin-orbital electronegativity, as represented by these SCF- $X\alpha$ orbital energy eigenvalues, and catalytic activity, one must

make use of the following concept.¹⁷ For a concerted chemical reaction to occur with reasonable activation energy, electrons must be able to flow between the reactants from the highest occupied molecular orbitals (HOMO) into the lowest unoccupied molecular orbitals (LUMO) with which they have positive, symmetry-conserving¹⁸ overlap, as the reactants move along the reaction coordinate. An effect of the large exchange splitting in the iron clusters is to raise the minority spin d orbitals to higher energies in comparison with the non-spin-polarized limit, effectively reducing the orbital-electronegativity difference and enhancing covalent overlap between the cluster HOMO (those symmetry-conserving minority-spin orbitals in the vicinity of the Fermi energy) and the LUMO of molecules such as N_2 , CO, and O_2 . Because the latter molecular orbitals are antibonding, overlap and concomitant reduction in the activation energy for effective electron flow between the iron HOMO and reactant LUMO should promote dissociation of the reactant molecules, a precursor to their catalytic reactivity. Dissociation of N_2 , CO, and O_2 does indeed occur on iron surfaces at room temperature and low coverage. Further discussion of the combined use of orbital-electronegativity and orbital-symmetry concepts in elucidating catalytic activity will be found in Ref. 8.

One may also compare the SCF- $X\alpha$ -SW orbital energies of a Pt_{13} cluster previously shown to exhibit most of the characteristics of the bulk and surface electronic structures of crystalline platinum or small particles thereof.¹⁵ In contrast to iron, there is no exchange splitting of the platinum cluster d orbitals, corresponding to the nonmagnetic state of bulk platinum, and the intrinsically larger electronegativity of the platinum atom results in a higher effective orbital electronegativity of the platinum cluster. The inclusion of relativistic corrections to the electronic structure of the latter cluster, as described in Ref. 16,

increases its effective orbital electronegativity even further. Consequently, the d orbitals around the Fermi level of the platinum cluster, although high in density, are poorly matched in energy and orbital electronegativity to the LUMO of N_2 and CO. Thus a high density of states around the Fermi energy is not a sufficient condition for catalytic activity. These theoretical results are consistent with the experimental fact that platinum, which is an excellent catalyst for some reactions, is inactive in promoting N_2 and CO dissociation and is a poor catalyst for ammonia and Fischer-Tropsch syntheses.

Dissociation of O_2 , the rate-limiting precursor to oxygen chemisorption and surface oxidation, occurs rapidly at relatively low temperatures and pressures on iron surfaces, suggesting low activation energy. On platinum surfaces this process seems to be less facile, generally requiring more stringent conditions for activation, such as the presence of surface "steps" which play the role of active sites. Like the processes of N_2 and CO dissociation considered above, the relative activities of platinum and iron for O_2 dissociation can be rationalized in terms of the respective orbital electronegativities defined by the SCF- $X\alpha$ orbital energy eigenvalues for the corresponding clusters. The Fermi level of the Fe_{15} cluster, as well as that of other spin-polarized iron aggregates including crystalline α -iron, lies somewhat above the energy of the partially occupied π_g orbital of O_2 , implying that O_2 is effectively electronegative with respect to this metal. The resulting electrophilic addition of electrons to the antibonding π_g orbital will promote O_2 dissociation. In contrast, the Pt_{13} Fermi level lies below the π_g orbital, indicating that O_2 is formally nucleophilic with respect to this cluster. Therefore, under normal circumstances, electron transfer between O_2 and a platinum aggregate of "surface" is in a direction which should favor bonding rather than dissociation of this molecule. Nevertheless, a platinum site can be "activated" for O_2 dissociation by placing the former

in a low-coordination environment in which a strong ligand-metal antibonding interaction raises the energy (lowers the electronegativity) of the Pt symmetry-conserving HOMO with respect to the $O_2 \pi_g$ orbital, thus facilitating electron transfer from the metal to dioxygen. Such an environment is provided by the "edge" atoms on a platinum surface "step."

In an attempt to elucidate further the mechanism of ammonia synthesis on iron catalysts, we have also constructed theoretical models for the effects of "promoters" (substances which, added to the catalyst, enhance its activity), as well as models for the surface nitride which is formed upon dissociation of N_2 on iron.¹⁹ The principal effect of the promoter is electron donation to iron, which reduces the electronegativity difference and activation energy for electron transfer between the metal HOMO and N_2 LUMO (as compared with pure iron), thereby promoting N_2 dissociation. The dissociative chemisorption of nitrogen results in the formation of a surface nitride with an effective negative charge which, in a reducing atmosphere, should facilitate protonation of surface nitrogen atoms, the formation of N-H bonds, and ultimately ammonia synthesis. An analogous argument applied to the dissociative chemisorption of CO on iron leads one to conclude that the formation of an iron surface carbide should facilitate C-H bond formation and Fischer-Tropsch synthesis. Details of these theoretical studies, theoretical models for N_2 dissociation and ammonia synthesis on ruthenium and osmium catalysts, and the nature of catalyst-support interactions are the subjects of forthcoming papers.²⁰

INTERACTION OF HYDROGEN WITH TRANSITION-METAL SURFACES

The dissociative chemisorption and absorption of hydrogen by clusters of atoms representing the surfaces, interstitial sites, and small aggregates of catalytically active transition metals have been studied theoretically,

using the nonrelativistic and relativistic versions of the SCF- $X\alpha$ -SW method in conjunction with the concept of spin-orbital electronegativity.¹⁶ Results for hydrogen interacting with small clusters of the Group-VIII transition metals, nickel, palladium, and platinum, indicate a splitting off of hydrogen bonding levels from the bottom of the d-bands, the bonding orbitals being the result of strong overlap between s,p,d-hybridized metal orbitals and the hydrogen 1s orbital. For the case of nickel, the 4s-like orbital component dominates the bonding with hydrogen, whereas the d-orbitals are dominant for palladium and platinum. These results are in agreement with recent interpretations of photoelectron spectra for hydrogen chemisorbed on and absorbed in such metals. They are also consistent with the close similarity of palladium and platinum, as compared with nickel, in regard to catalytic reactions involving hydrogen. The participation of various orbital components in the metal-hydrogen bonding can be understood fairly simply in terms of the relative values of the cluster orbital electronegativities for nickel, palladium, and platinum in relation to the hydrogen 1s orbital electronegativity. The results underscore the danger of making general statements about the dominance of s-orbital interactions over d-orbital interactions in hydrogen chemisorption and catalytic activity exclusively on the basis of theoretical studies of first-row transition metals, as has recently been done by some workers in the published literature. The almost perfect matching of the cluster d-orbital electronegativities of palladium to the hydrogen 1s orbital electronegativity suggests purely covalent Pd(4d)-H(1s) bonding. The strength of a heteronuclear chemical bond (as described by Pauling) can be viewed as having both covalent and ionic components in general. Moreover, the solubility of an impurity in a metal generally decreases with increasing electronegativity difference between solvent and solute (as originally described by Hume-Rothery), other

factors such as size factor being taken into consideration. Thus the minimization of electronegativity difference and ionic contributions in the bonding of hydrogen to palladium aggregates is consistent with the high solubility of hydrogen in this metal. It is also consistent with criteria based on moderate metal-adsorbate bond strength for the generally higher catalytic activity of palladium for reactions involving hydrogen, relative to the activity of nickel.

ELECTRONIC STRUCTURE AND SURFACE CHEMISTRY OF ALLOYS

It is well established that Group IB-VIII alloys such as Cu-Ni exhibit catalytic activities and corrosion passivities which are strong functions of composition. This behavior has been attributed to (1) the effects of electron configuration, (2) the effects of surface segregation, and (3) the formation of thin passive films such as chemisorbed oxygen. Bimetallic (and multimetallic) clusters based on Group VIII and IB metals also constitute the active centers of some commercial heterogeneous catalysts. To develop a more quantitative understanding of the relationship between the surface chemistry of such alloys and their electronic structures, we have begun SCF- $X\alpha$ studies of these systems, focussing on the electronic structures of bimetallic clusters which simulate the local molecular configuration of the bulk and surface environments.²¹ The advantage of this approach over conventional crystalline band models of alloying is that one can systematically study alloy electronic structure and surface properties such as chemisorption as functions of local composition and geometry, thereby circumventing the problems associated with long-range disorder.

Preliminary SCF- $X\alpha$ results for Cu-Ni alloys in the dilute nickel limit show the onset of significant Ni d-orbital hybridization with the delocalized

Cu s,p-like orbitals at the Fermi energy, analogous to the virtual bound d-orbital states at the Fermi level postulated by Friedel for dilute Ni impurities in bulk copper. Local densities of states have been generated from the discrete orbital energies of the Cu-Ni clusters, and the results are in good agreement with photoelectron spectra measured for Cu-Ni alloys in the Cu-rich limit by Spicer and co-workers. These theoretical results are a striking confirmation of the conjecture that short-range order and local chemical bonding dominate the electronic structure of binary solid-solution alloys in the limit of dilute solute concentration. The presence of nickel d-orbital delocalization onto surrounding copper atoms at the Fermi energy has important implications on the chemisorption and reactivity of molecules on Cu-Ni alloy surfaces, e.g., the formation of passive oxide films on Cu-Ni surfaces characterized by isolated Ni atoms or Ni "islands" embedded in the environment of surface-segregated copper atoms. More extensive cluster models for the surface chemistry, e.g., corrosion passivity and catalytic activity, of Cu-Ni alloys as functions of local composition and structure are currently under investigation.

Among the most interesting and significant results obtained thus far from these theoretical studies are the effects of alloying on local spin polarization and magnetic properties. For example, spin-unrestricted SCF-X α calculations for Cu-Ni alloys in the dilute nickel limit indicate that the local magnetic moment of a Ni site is quenched by the copper environment, whereas in dilute Cu-Fe alloys a strong local magnetic moment of the Fe sites remains, the magnitude of which depends on the ligand-field splittings of the Fe d-orbitals. The latter result is important since Fe impurities in a copper crystal constitute a Kondo system. The possible implications of the local magnetic properties of alloys on their surface chemical behavior are under investigation.

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